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Historical Perspective and Contribution of U.S. Researchers Into the Field of Self-Propagating High-Temperature Synthesis (SHS)/Combustion Synthesis (CS): Personal Reflections

by James W. McCauley and Jan A. Puszynski

ARL-SR-163 July 2008

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14. ABSTRACT This report presents an historical perspective and contributions of U.S. researchers into the field of Self-Propagating High-Temperature Synthesis (SHS)/Combustion Synthesis (CS) and personal reflections of the authors from about 1976 to the present for a special meeting in Chernogolovka, Russia – SHS-40 – celebrating 40 years of SHS research (International Conference on Historical Aspects of SHS in Different Countries, 22–27 October 2007, Chernogolovka, Russia). The review is presented in the context of the pioneering publication of Merzhanov, Skhiro, and Borovinskaya in 1967 and their subsequent activities. Included in the appendices are the power point charts used by the authors: part 1 by McCauley describes work in the U.S. from 1976 to 1996 and part 2 by Puszynski similarly for 1996 to the present.						
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1. Introduction

In 1967, Merzhanov, Skhiro, and Borovinskaya published the first comprehensive paper describing the self-sustaining character of reactions in a condensed phase, which could be utilized for synthesis of many ceramic and intermetallic materials (*1*). In this paper, the authors demonstrated the principle of so called "solid flame" using reactions between transition metals and boron, carbon, or nitrogen. The world-wide combustion synthesis community considers this a comprehensive paper and subsequent integrated experimental and theoretical research effort conducted in the former Soviet Union as the beginning of a new approach and method of synthesizing advanced high temperature materials. The main research was conducted by many Russian scientists in the Branch of Russian Academy of Sciences in Chernogolovka under the leadership of Professors Merzhanov and Borovinskaya (*2–11*).

During that period of our history, free exchange of information among scientists from different countries was very limited due to the cold war. The main source of information on research discoveries and accomplishments of Russian scientists available to U.S. and other researchers was through publications in Russian journals or their translated versions. Journals of Combustion, Explosion, and Shock Waves, Doklady Academy Nauk SSSR, Soviet Powder Metallurgy Metals and Ceramics, Inorganic Materials, and Doklady Physical Chemistry were the most searched journals in the area of combustion synthesis. In the early 1990s, a new International Journal of Self-propagating High-temperature Synthesis was created and has been published quarterly since its inception.

Self-propagating high-temperature synthesis (SHS), also called combustion synthesis (CS), is the exothermic process in which the reaction between two or more solid reactants or gas and condensed reactants takes place in a self-sustaining regime leading to the formation of solid products of a higher value (*12–14*). During the past forty years, hundreds of different compounds, including, nitrides, borides, carbides, silicides, sulfides, phosphides, hydrides, and oxides of many elements as well as intermetallics, composites, nonstoichiometric compounds, and solid solutions were successfully synthesized by this method (*12–18*). Some materials have been successfully scaled-up and produced by industry. To this group of materials, among others, belong: carbides of titanium, zirconium, tungsten, tantalum, boron and silicon, titanium diboride, molybdenum disilicide, aluminum nitride, silicon nitride, nickel aluminides, titanium nickelide, zirconium aluminides, and number of composites (e.g., TiC-TiB_2 and SiC-Si_3N_4) or solid solutions such as SIALONs and aluminum oxynitride (AlON).

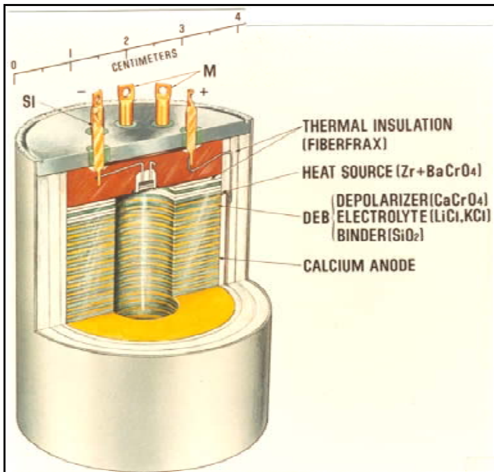
2. Review of Early Research in the United States and Western Countries

An historical perspective on research in the area of exothermic reactions occurring in a self-sustaining regime was well documented by Hlavacek (*19*) and McCauley (*16*). In the United States, the first reported research utilizing self-sustaining character of condensed-phase reactions was conducted by Walton and Poulos (*20*) in the mid and late 1950s. These authors explored thermite reactions to make refractory coatings. Mixtures of aluminum and/or magnesium with oxides of iron, cobalt, and vanadium were used to produce different cermets. The authors also explored the combustion synthesis of silicides, borides, and carbides. The use of beryllium as a reducing agent and reduction of uranium oxide were discussed. Several other researchers made attempts to synthesize other materials like aluminum phosphide by direct reaction between red phosphorous and aluminum powders (*21*), tantalum metal by reduction of K_2TaF_7 by sodium (*22*), the formation of molybdenum disilicide by direct reaction between molybdenum and silicon powders (*23*). In 1964, Krapf (*24*) patented the chemical hot press in which a mixture of reactive powders was heated in a die by passing an electric current. After initiation of exothermic reaction, the product was pressed by an uniaxial force. The concept of pressing hot products generated in strongly exothermic reaction was also described in 1967 by Stringer and Williams (*25*). According to these authors, reaction pressing can be applied to intermetallic and metal-metalloid compounds generated by fast evolution of energy due to a chemical reaction between reactant powders. They claimed that the exothermic effect of reaction in many cases is sufficient to form a plastic product mass, which can be quickly formed to different shapes. The authors emphasized the use of aluminides, berrilides, titanides, zirconides, and borides. In 1968, McKenna (*26*) patented a process of preparing tungsten monocarbide utilizing exothermic effect generated during the reaction between elemental powders. In 1973, Hardt and Phung (*27*) published a very important paper on propagation of gasless reactions in solids, which further alerted U.S. scientists about importance of the combustion synthesis.

3. Combustion Synthesis Research in the United States After 1980

After sporadic activities in the Western World in the 1950s and 1960s, a more significant research effort was made in the United States starting in the early 1980s. In 1982, McCauley et al. (*28*, *29*) and Holt and Kingman (*30*) published new results in the area of combustion synthesis, which generated interest at several universities and U.S. government laboratories. The review paper on the SHS activities in the Soviet Union written by Crider (*31*) also stimulated the new interest. The work of McCauley et al. (*32*) was initiated from comprehensive investigation

of burning characteristics of zirconium metal with air and barium chromate for the potential use of this reacting system in thermal batteries (*16*, *32*). The basic schematics of a thermal battery and key gasless and gas-solid SHS reactions are shown in figure 1.



- $Zr + (AIR) \rightarrow ZrO_2$
- $Zr + BaCrO_4 + (AIR)$
  - $3\ Zr + 4\ BaCrO_4 \rightarrow 3\ ZrO_2 + 4\ BaO + 2\ Cr_2O_3$
    $3\ ZrO_2 + 3\ BaO \rightarrow 3\ BaZrO_3$
  - $3\ Zr + 2\ BaCrO_4 \rightarrow 3\ ZrO_2 + 2\ BaO + 2\ Cr$
    $3\ ZrO_2 + 2\ BaO \rightarrow 2\ BaZrO_3$

<u>HEAT OF REACTION:</u>

15 - 50 WT% Zr
85 - 50 WT% $BaCrO_4$ — 273-502 cal/g

502 cal/g for ~ 60 WT% $BaCrO_4$

Figure 1. Use of zirconium in thermal batteries (*16*).

Following this work on zirconium burning characteristics (*32*), McCauley and his co-workers (*28–29*, *32–37*) shifted their activities from using by-products of SHS to processing, focusing on the following: (i) utilize reaction sintering concepts without pressure; (ii) importance of physical and chemical characteristics of powders; (iii) focus on phase equilibrium; and (iv) detailed characterization of final sintered products.

Critical issues in reaction sintering are as follows:

- Chemical driving forces much higher than conventional sintering,
- If gas forms most diffuse out,
- Volume fractions of reactants and products change with time,
- Kirkendall effects: porosity formation due to density change between reactants and products,
- Wetting between liquids and solid phases becomes important, and
- Grain size reduction from reactants – nucleate new phases.

A pioneering work of Holt and Kingman (*30*) was mainly focused on combustion synthesis of ceramic powders and refractory materials in general, which was more aligned with the research activities conducted in the former Soviet Union's laboratories.

A turning point in the U.S. efforts in SHS was catalyzed by a major contract from the Defense Advanced Research Projects Agency (DARPA) that was carried out from 1984 to 1986. The overall contract manager was J. W. McCauley and the program manager was J. Birch Holt at the Lawrence Livermore National Laboratory with sub-contracts at The University of California, Davis, Ceramatec, Los Alamos National Laboratory, and Rice University.

The key universities, which started research in combustion synthesis in the early 1980s included: University of California at Davis, Georgia Institute of Technology, State University of New York at Buffalo, and Northwestern University. These early research activities were supported by the National Science Foundation, Department of Energy (Los Alamos National Laboratory and Sandia National Laboratory), and U.S. Army. Also, some research in the area of combustion synthesis was conducted in U.S. government laboratories, especially the Department of Energy, U.S. Army, and U.S. Navy. In table 1, the summary of research activities in academia, government laboratories, and industry in the U.S. at the end of 1980s is presented.

Table 1. SHS R&D groups in the U.S. in late 1980s.

Organization	Principal Investigators	Technology Focus
Department of Defense		
Army Materials Technology Lab.	Croft, Marzik, McCauley	Powder characterization; sintering; phase equilibria
Army Ballistic Research Lab.	Niller, Kottke	Dynamic compaction; modeling
Army research Office	Crowson	Coordination and management
Department of Energy		
Los Alamos National Laboratory	Behrens	High temp. chemistry; laser ignition; modeling
Lawrence Livermore National Lab.	Holt, Halverson, Chow	SHS; bulk materials, models
Sandia National Laboratory	Margolis	Modeling
Academia		
Alfred University	Spriggs	Materials processing; reviews
Oregon State University	Kanury	Modeling
Washington State University	Wojcicki	Materials processing; eutectics
University of California – Davis	Munir	SHS; materials processing; fundamentals
Northwestern University	Matkowsky	Mathematical analysis
Georgia Tech Research Institute	Logan	SHS; materials processing; thermites
Rice University	Margrave	High temperature mass spectrometry
New Mexico Inst. of Mining & Tech.	Thadani	Explosive compaction
State University of NY – Buffalo	Hlavacek and Puszynski	SHS; powders, mat'l processing; math, modeling
University of California – San Diego	Meyers	Explosive compaction
University of Florida	Clark and Dalton	Microwave processing
Colorado School of Mines	Moore	SHS, intermetallics
Industry		
Research Triangle Institute	Mullins	Fibers and metal matrix composites
CERAMETEC	Cutler	SHS; powders; thermites
General Sciences Inc.	Zavistanos	SHS densification
System Planning Corp.	Frankhouser	Reviews and analyses
Lockhead Corp.	Hardt	SHS, sintering; phase equilibria
Corning Glass Works	DeAngelis	Reactive hot pressing
W.R. Grace	Rice	Materials processing
Advanced Refractory Technologies	Blakely	SHS powders; whiskers
Innovative Materials, Inc.	Puszynski and Hlavacek	SHS, nitride, boride, and carbide ceramics;
Benchmark Structural Ceramics	Hida	intermetallics
Powder Technologies, Inc.	Logan	SHS powders and whiskers
Synergetic Materials, Inc.	Halverson	SHS powders and bulk materials
Kiser Research, Inc.	Kiser	Advanced materials
		Soviet SHS technologies

Both theoretical and experimental efforts were undertaken to explain various phenomena of combustion synthesis. Theoretical research describing combustion front stability and bifurcation analysis was done by Matkowsky from Northwestern University, and Margolis, Armstrong and Koszykowski from Lawrence Livermore National Laboratory. Professor Matkowsky has published numerous theoretical papers on the subject of gasless and gas-solid reactions (*38–52*). His pioneering work with Margolis, Kaper, and Leaf on bifurcation on pulsating and spinning reactions in condensed two-phase combustion belongs to very fundamental classics of combustion synthesis (*39*). His further analysis with Bayliss of two routes to chaos in condensed phase combustion as well as series of theoretical papers on filtration combustion with Booty and scientists from Chernogolovka, Russia made very significant contributions to better understanding of complex nonlinear phenomena in combustion synthesis. Very accomplished mathematicians and theoreticians such as Shkadinsky, Shkadinskaya, Aldushin, and Volpert from Russia cooperated closely with Professor Matkowsky during the 1990s. Dr. Volpert joined Northwestern University and he presently works there as a professor of applied mathematics. Professor Volpert published several papers with Professor Matkowsky on the theory of gasless reactions and various aspects of filtration combustion in porous structures with and without deformation. He also contributed to better understanding of combustion in microgravity environments and mathematical modeling of frontal polymerization and understanding of wave propagation during free-radical polymerization with the gel effect (*53–63*).

A parallel mathematical modeling effort was undertaken at the State University of New York at Buffalo under the leadership of Professor Hlavacek, who joined that university in 1981. Professor Hlavacek established a very active research group, which focused its research on both experimental studies and mathematical modeling of self-sustaining reactions and materials engineering aspects of combustion synthesis. Due to the access to parallel computer processors in mid 1985, his research modeling team was able to simulate complex combustion patterns, including transition to chaos, breaking of symmetry, fingering effects, multiple spinning waves in two and three dimensions, as well as complex behavior of the combustion front during gas-solid reactions (*64–76*). Figure 2 shows the transition to chaos via period doubling in gasless reacting systems. A typical sequence of spinning combustion waves in two dimensions is shown in figure 3. It should be noted that these simulations were done using a very sophisticated adaptive mesh computer program, which allowed completing calculations on available supercomputers within a reasonable period of time. This computer technology looks old today, but truly it was the state-of-the-art 20 years ago.

In the 1990s, Professor Law from Princeton University published a number of papers describing model formulations, mathematical modeling of combustion front propagation and comparison of key combustion characteristics with experimental results (*77–87*). Figure 4 shows comparison of experimental and theoretically predicted combustion limits for the Co-Ti system (*82*).

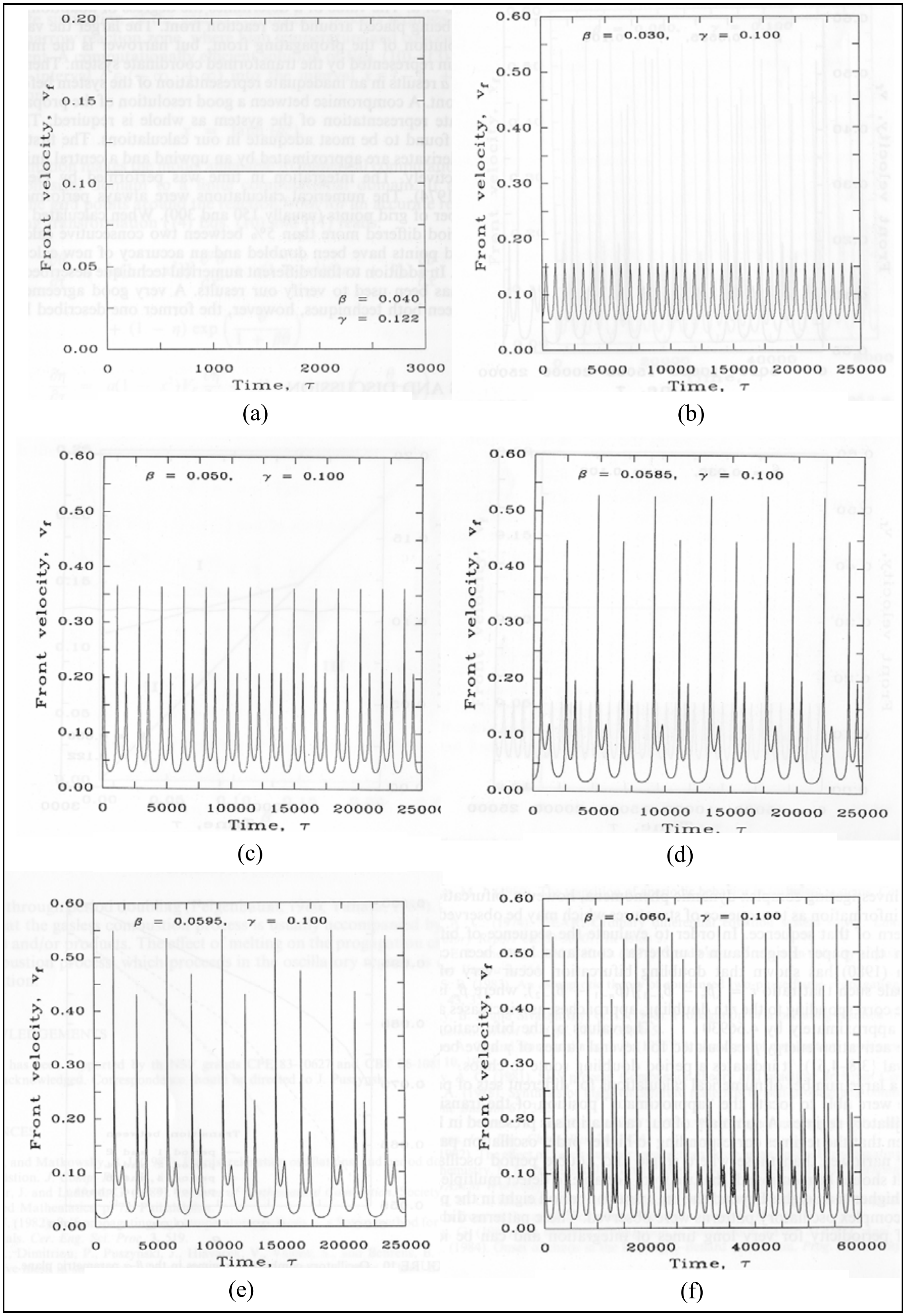


Figure 2. Combustion front propagation velocity in gasless systems vs. time with different dimensionless activation energy and heat of reaction (*74*).

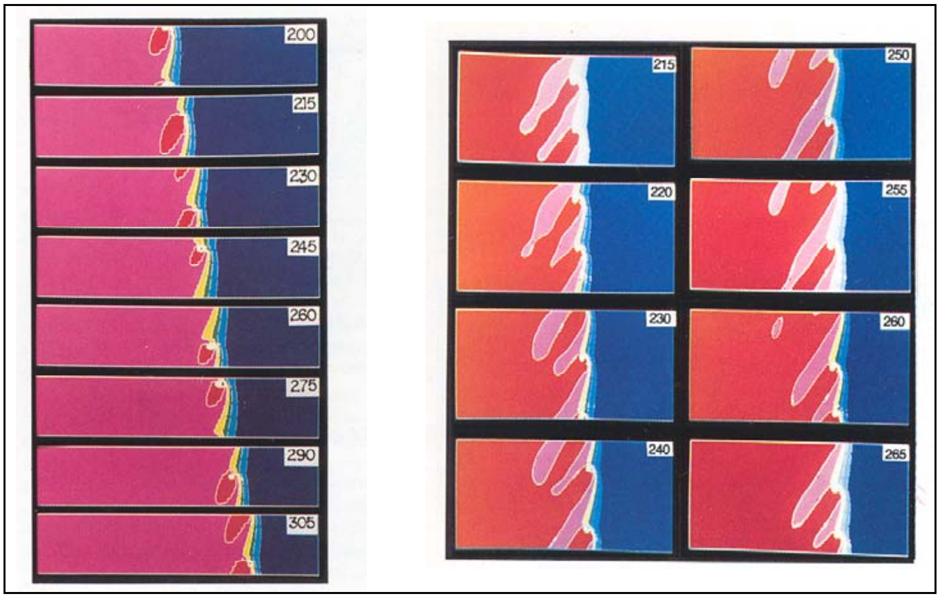


Figure 3. Two-dimensional modeling: (a) single head spinning wave; (b) multiple head spinning waves (*70*).

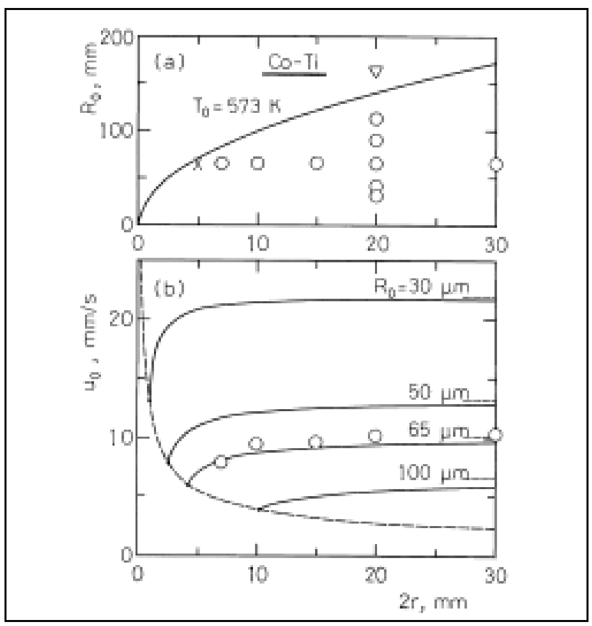


Figure 4. Nonadiabatic combustion behavior for Co–Ti system with stoichiometric mixture at $T_0 = 573$ K. (a) Range of flammability as functions of 2r and R_0; experimental data; (○) designates the steady propagation, (▿) the flame extinction during the propagation, and (×) the non-ignition. (b) Burning velocity u_0 as a function of 2r, with R_0 taken as a parameter; data points are experimental in the literature (*82*).

During the same period of time, other researchers from various universities also contributed to development of new reaction models and mathematical modeling of combustion synthesis processes. Contributions by Professors He and Stangle (*88*), Kanury (*89*), Bhattacharya (*90*), and Varma (*91*) are also of very significant importance.

The experimental research conducted in the U.S. national laboratories and universities resulted in many accomplishments, which led not only to significant contributions into the fields of physics, materials science, ceramic engineering, and reaction engineering but also to the development of several technologies, which resulted in their commercialization.

In academia, Professor Munir, one of the key SHS leaders in the United States, has been involved in the area of combustion synthesis from the early 80s. His research activities at University of California at Davis resulted in education of large number of excellent scientists who are working in many countries. His selected major research contributions are listed next (*92–105*):

- Combustions synthesis of refractory carbides, borides, silicides, nitrides and intermetallic compounds (1980s).
- Analysis of the role of thermal migration in pore formation during SHS synthesis (1990).
- Theoretical analysis of the stability of self-propagating combustion synthesis waves, concept of SHS diagrams (1990–1992).
- Use of the Boddinton-Laye mathematical analysis for direct determination of kinetic parameters during SHS (1992).
- Analysis of the origin of porosity in SHS products (1993).
- The role of electric fields in SHS reactions: Modeling and experimental work (1995–1998).
- Separation of the thermal (Joule heat) from the intrinsic (electron wind effect) contributions of the field (current), work on electromigration has demonstrated field effect on point defect generation and mobility (2001).
- Recent work on the combined mechanical and field activation to synthesize dense (bulk) nano-ceramics and nano-composites in one step (2001–present).
- Use of field activation for simultaneous synthesis and consolidation of complex materials; Ti_3SiC_2 (1999), TiB_2-WB_2-CrB_2 (2001), AlN-SiC (1996–2000).
- Use of field activation for microalloying (2003–2004).
- Use of field activation to prepare nanostructured functional oxides for fuel cell applications: Novel demonstration of power generation at room temperature by protonic conduction.

The main advantage of the field-assisted process is the electrical discharge at particle contacts, which promote sintering. Numerous materials, including TiN, TiO_2, SiC, Si_3N_4-TiN, ZrO_2-Al_2O_3, and FeAl were sintered during the past several years resulting in the formation of dense articles with nanosize grains. The starting powders were obtained by plasma, mechanical alloying, or sol-gel techniques. A very important modification of this field-assisted technique was presented by Munir (*93*). It was demonstrated that the combination of field-assisted technique, such as SPS, and in-situ synthesis of materials from nanoreactants or mechanically-activated powders may result in the formation of desired phase and consolidated products retaining nanostructure. Experimental results did show that the presence of electrical field influences the mechanism and rate of the condensed phase reaction as well as the phase composition and elemental distribution in solid solutions. The main effects of the electric field during the reaction have been attributed to Joule heating, enhanced mass transport by electron-migration, and the formation of plasma on the particle level. Therefore, the entire process of in-situ densification of combustion synthesized bulk materials exhibiting a nanostructure can be divided into three steps:

- Mechanical activation of participating reactants,
- Cold compaction of pre-alloyed powders, and
- Field-activated pressure-assisted synthesis.

In the first step, reactant powders are mixed in a stoichiometric ratio and co-milled in a planetary mill in order to form nanocrystallites. During the milling the particles are flattened, fractured, and welded. This process of grain size reduction, generation of residual stresses, and phase transformation has a significant effect on the kinetics of combustion reactions during the final consolidation step in the presence of electrical field.

The second step involves cold-compaction of mechanically activated powders into a graphite die. The final step includes simultaneous application of electric current and uniaxial pressure under an inert atmosphere. In this step, the combustion reaction is initiated by Joule heating and the hot product is densified within a few minutes. Relative densities between 90% and 100% of the theoretical density can be commonly achieved.

It should be mentioned that Professor Munir has published many papers and obtained numerous patents for his innovations of combustion synthesis. In this review, only few selected papers are mentioned (*92–105*). He has also made very important contribution to the SHS community by reviewing articles on SHS for many journals, including the Ceramic Bulletin, and Materials Science Reports, which are cited by thousands and continue to be cited to the present. Professor Munir has established among U.S. scientists the strongest collaboration with researchers around the world. He has collaborated with Professors Frederic Bernard, University of Burgundy, Dijon, France; Manshi Ohyanagi, Ryukoku University, Seta, Japan; Umberto Anselmi-Tamburini,

University of Pavia, Italy; Giacomo Cao, University of Cagliari, Italy; Manfred Martin, University of Aachen, Germany; Rainer Telle, University of Aachen, Germany; In-Jin Shon, Chonbuk National University, Korea; Myeong-Woo Cho, Inha University, Korea; Roberto Tomasi, Sao Carlos Federal University, Brasil; Qing-sen Meng Taiyuan University of Technology, China; K. A. Khor, Nanyang Technological University, Singapore.; Z. Y. Fu, Wuhan University of Technology, China; and Yu. Maksimov, Tomsk University, Russia. He has also ongoing collaboration with U.S. national laboratories, including collaboration with Dr. Alex Gash from Lawrence Livermore National Laboratory and Dr. John Neal from Oak Ridge National Laboratory. Professor Munir has published many papers and he was awarded with numerous patents related to combustion synthesis. In 1993, he established the American Consortium of Combustion Synthesis.

The State University of New York at Buffalo (SUNY/Buffalo) was the second university strongly involved in combustion synthesis research. As indicated before, Professor Hlavacek built a very large group of Ph.D. students and research scientists. His integrated approach resulted in a strong development of combustion synthesis technologies supported by strong basic experimental research and mathematical modeling programs (*106–117*). In the mid 1980s, Drs. Hlavacek and Puszynski successfully transferred the technology of synthesizing aluminum nitride by combustion synthesis technique into Advanced Refractory Technologies Company located in Buffalo, NY. This company was the first to produce aluminum nitride by this technique. In the late 1980s, other technologies for synthesis of silicon nitride, titanium carbonitride, α- and β-sialons, titanium carbide-titanium boride and silicon nitride-silicon carbide composites as well as tungsten carbide and aluminum phosphide were developed by Drs. Hlavacek and Puszynski. The university spin-off company Ceramic Materials Processing, Inc. was involved in manufacturing of ceramic and intermetallic powders by the SHS method, scale-up of combustion reactors, and technology transfer. During the 1980s and early 1990s, several researchers visited SUNY/Buffalo. Dr. Puszynski joined Professor Hlavacek's group in 1982. In 1991, Puszynski accepted a position at the South Dakota School of Mines and Technology where he has been continuing SHS-related work. His research has been focused on combustion synthesis of nanopowders and nanocomposites as well as the reaction kinetics in systems consisting of nanosize reactants (*118–126*). Professor Puszynski established close cooperation with Yerevan State University in Armenia, Academy of Mining and Metallurgy in Cracow, Poland and several U.S. national laboratories. His recent work indicates that various intermetallic composites reinforced with single wall carbon nanotubes can be formed in a self-sustaining regime with the ultimate grain structure being at the nanoscale (see figure 5). His comprehensive work on combustion synthesis in the Si-Al-Ti-O-N-C system has led to the formation of many complex compounds with different morphologies and phase compositions. His work on chemically-assisted gas transport combustion synthesis led to successful synthesis of nanosize silicon carbide. Figure 6 shows inert gas pressure regimes where silicon carbide can be formed. Figure 7 shows different morphologies of silicon nitride formed with and without the presence of gas-transport promoting additives.

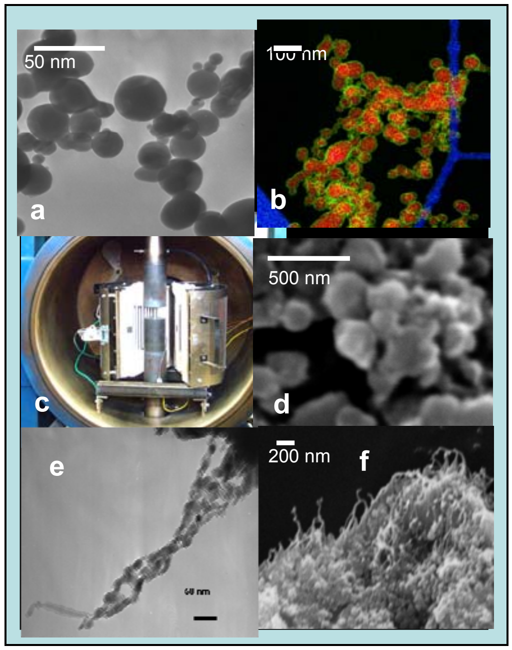
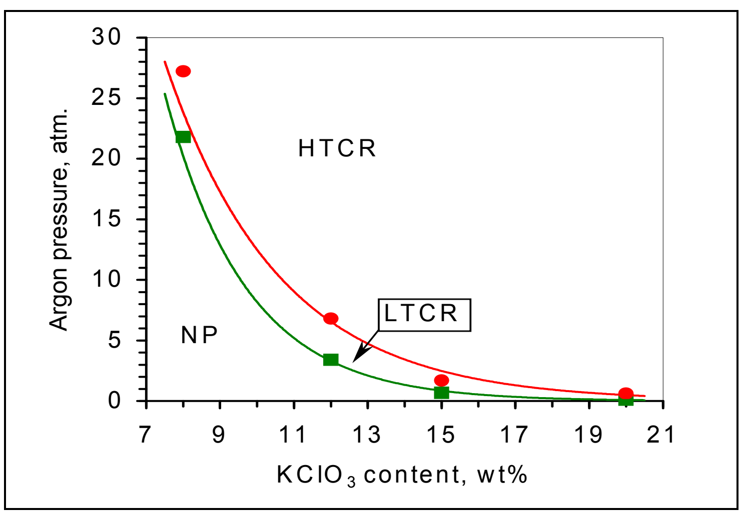
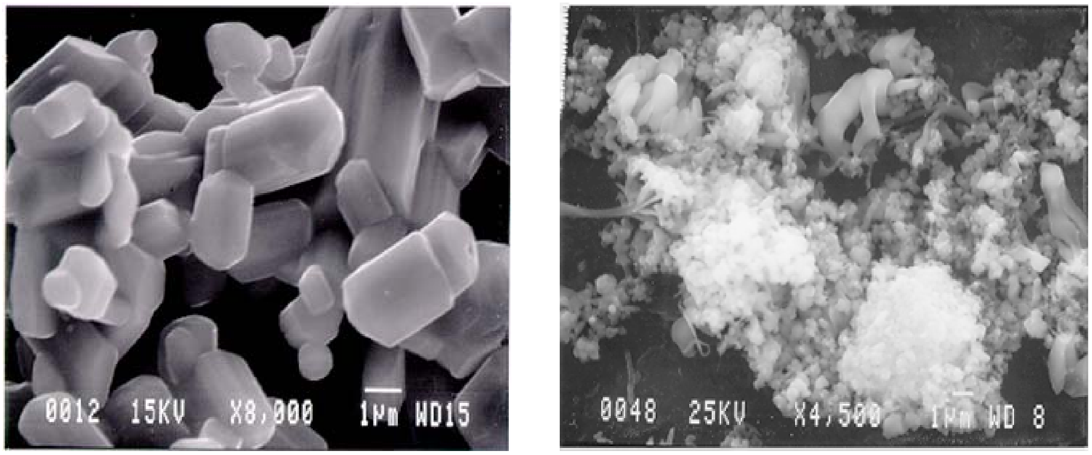


Figure 5. (a) and (b) TEM images of Al and Ni nanoreactants, (c) reaction chamber, (d) SEM image of nanosize nickel aluminide-alumina composite prepared by simultaneous combustion synthesis and densification, (e) and (f) SEM images of single-walled carbon nanotubes reinforced nickel aluminide-alumina nanocomposites.



Note: NP: no propagation; LTCR: low-temperature combustion regime; HTCR: high-temperature combustion regime.

Figure 6. Combustion propagation diagram in Si-C-$KClO_3$ reacting system (*120*).



(a) (b)

Figure 7. SHS synthesized (a) β-Si_3N_4 and (b) α- Si_3N_4 (*122*).

Professor Puszynski has been actively involved in the organization of technical sessions dedicated to combustion synthesis at various conferences, including the American Institute of Chemical Engineers and the American Ceramic Society. Professor Puszynski also serves as a frequent reviewer of journal manuscripts. He also serves as a consultant to Noveltec company in Tennessee, which is involved in production of variety products, including sialons, carbides, borides, nitrides, and sulphides by the SHS technique.

Dr. Viljoen spent several years at SUNY/Buffalo in the late 1980s and early 1990s. His work in the SHS area was focused on fundamental aspects of combustion reactions involving the solid state. After accepting a professor position at the University of Nebraska he continued his fundamental work focusing on solid-solid reactions with mechanical coupling, understanding of solitons and non-equilibrium reactions in solid phases, combinatorial approach to surface contacts in solid-phase reactions, and analysis of the effect of heat transfer on combustion front propagation limits (*127–131*). Professor Viljoen also contributed to a better understanding of strongly exothermic reactions taking place under strong compression. He also cooperated with Russian scientists, including Dr. Shteinberg, and he supervised several Russian graduate students who joined his research group.

Dr. Lis joined Professor Hlavacek's research group in the late 1980s. His research at SUNY/Buffalo was focused on combustion synthesis of silicon-nitride-silicon carbide composites and sialons. He published jointly with Professor Hlavacek and his key staff several papers, which outlined key aspects of combustion synthesis, processing, and sintering of SHS synthesized materials. After his return to Poland he continued building SHS related programs together with his former Ph.D. advisor, Professor Pampuch. Later on, the group headed by Professors Pampuch and Lis became one of the most active European groups outside the former Soviet Union.

It should be clearly noted that Professor Hlavacek educated many excellent Ph.D. students who are currently working in the industry or academia. He also was the pioneer who introduced many chemical engineers into the field of combustion synthesis.

In the late 1980s and early 1990s, several other U.S. universities got involved in combustion synthesis research. In the early 1990s, Alfred University, under the leadership of Drs. Spriggs and McCauley, initiated a research program focusing on further development of SHS technologies. With the strategic hiring of Dr. Stangle several R&D initiatives were conducted, including: (1) fabrication of dense $MoSi_2$ and $MoSi_2$-based composites using SHS process; (2) combustion synthesis and fast-firing of nanocrystalline yttria-stabilized zirconia; (3) fabrication of functionally gradient materials by SHS method (see figure 8 [*156*, *157*]); (4) development of a centrifugal-SHS process and analysis of its fabrication capabilities; (5) investigation of the mechanism and kinetics of combustion synthesis; and (6) study of the combustion synthesis process for materials fabrication. This multi-year research program resulted in 31 publications and international recognition of an established research center (*132–162*).

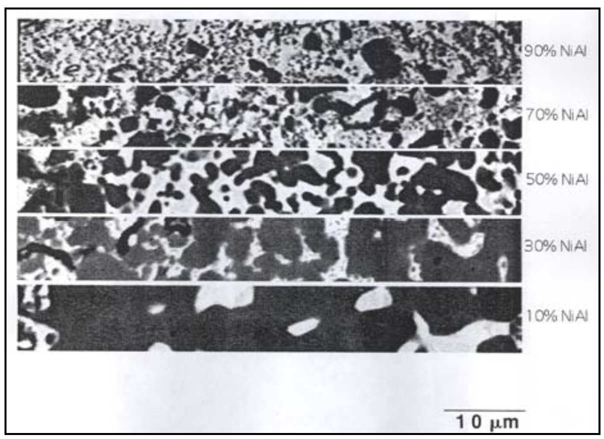


Figure 8. Functionally-graded materials made by SHS (*156*, *157*).

In addition, the Alfred group established several international collaborations:

- Interactions and formal agreement with NRIM, Japan (Kaieda),
- Formal agreement with the Institute of Materials Science, School of Mining and Metallurgy, Poland (Pampuch), and
- Interactions and formal agreement with ISMAN (Merzhanov and Borovinskaya).

At approximately the same time period, Professor Varma initiated combustion synthesis research at Notre Dame University. His initial research interest was focused on mathematical modeling of combustion fronts. However, very quickly his research evolved toward experimental

investigation of reaction kinetics of heterogeneous reactions as well as understanding of system heterogeneity and melting effects on propagation of combustion fronts in the condensed phase (*163–177*). Professor Varma invited a few Russian scientists, including Drs. Mukasyan and Rogachev to work with him at Notre Dame University. He also attracted several graduate students, including some from Russia. Dr. Mukasyan was offered a permanent position at this university and he is still working there conducting his own research program in the area of combustion synthesis. A few years ago, Professor Varma accepted a new challenging position at Purdue University where he continues research in the area of strongly exothermic noncatalytic reactions. Both Professors Varma and Mukasyan, when working together at Notre Dame University, conducted combustion synthesis research in a microgravity environment. They also investigated possibilities of synthesizing biomaterial using the SHS technique. They also initiated work on combustion solution of oxide nanomaterials for development of catalysts.

Presently, Professor Mukasyan is actively continuing that research. A variation of the combustion synthesis process, namely utilization of exothermic redox reactions in solutions, was already investigated by several researchers in India and the U.S. Professor Bhaduri was among the first who explored this technique in the U.S. (*178–182*). This type of the reaction is called solution combustion synthesis (SCS) and involves a self-sustaining reaction between metal nitrates and carbonaceous fuels, such as urea, glycine, or carbohydrazide. The reaction between such fuel and oxygen containing species results in a significant heat generation. In practice, this process is accomplished by dissolution of metal nitrates and uniform mixing of the fuel and nitrates in water, preheating of the oxidizer-fuel solution with subsequent water vaporization, followed by self-ignition of the dry reactants. As a result, the formation of crystalline oxide nanopowders with tailored compositions can be formed. The main advantage of this approach is mixing of reactants at the molecular level. The overall reaction process is very fast and results in the formation of nanograins exhibiting a high purity due to vaporization of all volatile species at high reaction temperatures generated by this exothermic reaction. Another important advantage of this method is a possibility of the formation of complex oxide nanopowders for different applications as structural ceramics, catalysts, bio-or fuel cell materials (*183–188*).

The combustion synthesis research at Colorado School of Mines has been carried out by Professor Moore for almost 20 years. Professor Moore’s research interest has been on the formation of composite materials at normal or reduced gravity environments. The recent research interest of Professor Moore is focused on the formation of biomaterials (*189–192*). Professor Moore is very actively involved in numerous professional societies and his published contributions into the field of SHS are highly regarded by the international SHS community.

A significant research effort in the U.S. was focused on simultaneous combustion synthesis and hot pressing. Professor Logan from Georgia Institute of Technology established an experimental program focusing on densification of titanium diboride and various composites generated during aluminum thermal reduction of oxides (*193*). Professor Logan developed a strong cooperation

with the R&D group led by Dr. Niiler from U.S. Army Ballistics Laboratory and McCauley of the U.S. Army Materials Technology Laboratory. Niiler and his co-workers were involved in shock densification of combustion synthesized materials by means of explosives (*194*, *195*).

Shock-induced densification of ceramics and cermets by unique high speed forging was conducted by Professor Meyers and his research group at University of San Diego, CA (*196–211*). Professor Meyers contributed to elucidation of the reaction mechanism at the front in Ti-C system. This work was done with Dr. La Salvia from the U.S. Army Research Laboratory and produced some outstanding results describing the physicochemical mechanism of that reaction (*199*, *200*). Professor Meyers also contributed to fundamental understanding of densification by quasi-isostatic pressing (QIP) of reaction products. This work was done in collaboration with Professor Olevsky (*210*, *211*). The use of a granular pressure transmitting medium, initially introduced at Chernogolovka, was used to produce TiC plates with dimensions of 12 × 12 × 2 in. Production and densification of TiC-NiTi cermets was another accomplishment of this technology. Figure 9 shows a typical microstructure of TiC-25%Ni composite material formed by SHS dynamically densified material.

Professor Meyers collaborated with Dr. Kim, South Korea, Professor Meyer, Chemnitz University, Germany, Dr. Ramas Raman from Ceracon, Professor Olevsky, San Diego State University, and Dr. Jamet from Ecole Centrale de, France.

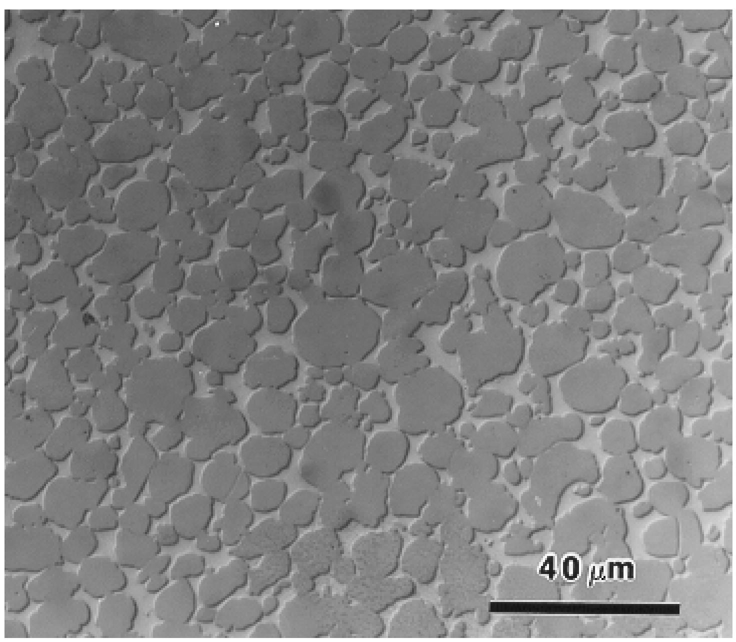


Figure 9. Microstructure of in-situ densified TiC-25%Ni composite formed during combustion synthesis and obtained in Professor Meyers' laboratory.

A significant contribution into the area of shock densification of combustion synthesized intermetallics and ceramic materials was also made by Professor Thadani (*212–217*).

Recently, Professor Luss and his co-workers developed a novel efficient synthesis method called Carbon Combustion Synthesis of Oxides (CCSO) for production of advanced nano and submicron complex oxides such as ferroelectrics ($BaTiO_3$, $SrTiO_3$), hard and soft magnetic materials (Ba, Sr, Pb Mn-Zn and Ni-Zn ferrites), superconductors (Y123), optoelectronics (ZnSnO), solid-oxide fuel cell components ($LaGaO_3$), battery electrodes ($LiMn_2O_4$), catalysts, membranes, and digital pigments (*218–221*). The method is a modification of SHS that uses carbon as the heat generating fuel instead of a pure metal. The concentration of the carbon in the reactant mixture enables control of the moving front temperature and average temperature front velocity as well as the products particle size and surface area. CCSO may be used to produce oxides even when SHS cannot be applied, such as when the pure metal is pyrophoric (such as Li or La) or that it melts at room temperature (for example, Ga), or when the metal heat of combustion is relatively low. In contrast to the common SHS, the combustion product (carbon dioxide) is not incorporated into the product and exits from the sample. Moreover, the lubricating properties of the carbon enhance the mixing by ball milling. The high rate of CO_2 release increases the porosity of the particles and the friability of the powder. The process is significantly faster than common calcinations processes and produces powders with smaller particle size.

Another interesting activity conducted by this group is focused on spontaneous magnetization generated by solid state combustion (*222–228*). Using a highly sensitive high-T_c superconducting quantum interference device (SQUID), they were able to conduct the first measurement of the very low intensity (order of nT) transient magnetic field formed by a combustion front motion. The front propagation generated a slowly oscillating magnetic field on which, in some cases, high frequency small oscillations were superimposed. The magnetic power spectra of the oscillations scaled as a power law, suggesting that they are associated with a stochastic process. The combustion synthesis of ferrites generated qualitatively different magnetic fields under different modes of combustion front motion, i.e., planar, spin, and pulsating. The average magnetization vector generated by either planar or pulsating combustion was oriented at a smaller angle with respect to the pellet axis ($\phi \leq 45°$) than those generated by spin combustion ($60° \leq \phi \leq 80°$). The Earth's magnetic field had no impact on the spontaneous magnetization field of the samples. Dr. Luss' research group also developed a simple electromagnetic model which predicted the qualitative features observed in the experiments. The transient evolution of this field depends on whether the combustion temperature exceeds or does not exceed the Curie temperature.

Figure 10 shows a case in which a residual magnetic field of about 4 μT was generated by the spontaneous magnetization of the ferromagnetic product $PbFe_{12}O_{19}$ in the post-combustion zone. The characteristic spontaneous magnetic field saturation time of about 250 s was much longer than the 1–2 s duration of the electrical signal. The magnetic field was created by three different mechanisms: (1) orientation of the magnetic dipole moments by internal electrical field force, (2) dipole self-orientation along existing residual field of the bulk material during the cooling, and (3) via chemisorption of O_2 molecules on the ferromagnetic surface.

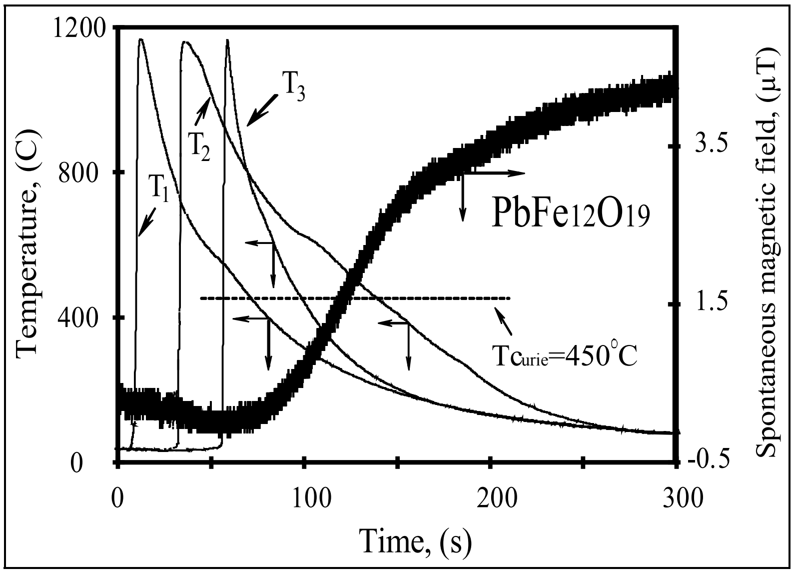


Figure 10. Three temporal combustion temperatures in the top (T_1), middle (T_2), and bottom (T_3) of the sample and the spontaneous magnetic field measured near the one side of the sample during the combustion synthesis of ferrite. The distance between surface and sensor was 10 mm (*226*).

During the past several years, another interesting technology was developed by Dr. Weihs from John Hopkins University (*229–231*). Multilayer reactive foils provide ideal sample geometries for studying different SHS reactions with a high level of contact between reactants. In addition, the thickness of each layer can be precisely adjusted. Currently, his technology is used by Reactive NanoTechnologies, Inc., in Baltimore, MD for bonding dissimilar materials and in other applications.

4. Summary

This review clearly indicated that the contribution of U.S. scientists to both theoretical understanding of combustion reactions in condensed phase and development of new innovative technologies based on the principle of self-propagating reactions between solid reactants or those involving solid and gas interactions is significant. Despite the relatively small number of researchers involved in this field, the number of publications, patents, as well as technological know-how development is quite impressive.

More than 40 years have passed since the discovery of SHS in 1967. It should be emphasized that, during the last 17 years, the exchange of information among all scientists working in combustion synthesis is without the political barriers that existed until the early 1990s. Every 2 years, researchers have the opportunity to present their results at international SHS symposia. New close-cooperation agreements have been established between different universities and research institutes. We hope that this trend will continue and new generations of scientists and engineers will contribute into the field of SHS freely and without any external constraints.

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Appendix A. Oral Presentations: Part 1

From the "International Conference on Historical Aspects of SHS in Different Countries," 22–27 October 2007, Chernogolovka, Moscow, Russia. Historical perspective and contributions of U.S. Researchers into the Field of Combustion Synthesis (SHS): Personal Reflections—1976–1996, James W. McCauley.

The viewgraphs in this appendix appear in their original form, without editorial change.

Historical Perspective and Contribution of U.S. Researchers into the Field of Combustion Synthesis (SHS):

Personal Reflections

Part 1: 1976–1996

James W. McCauley, Army Research Laboratory, U.S.

and

Jan A. Puszynski, South Dakota School of Mines and Technology, U.S.

SHS - 40
Research Center RAN
Chernogolovka, Russia
22-24 October 2007

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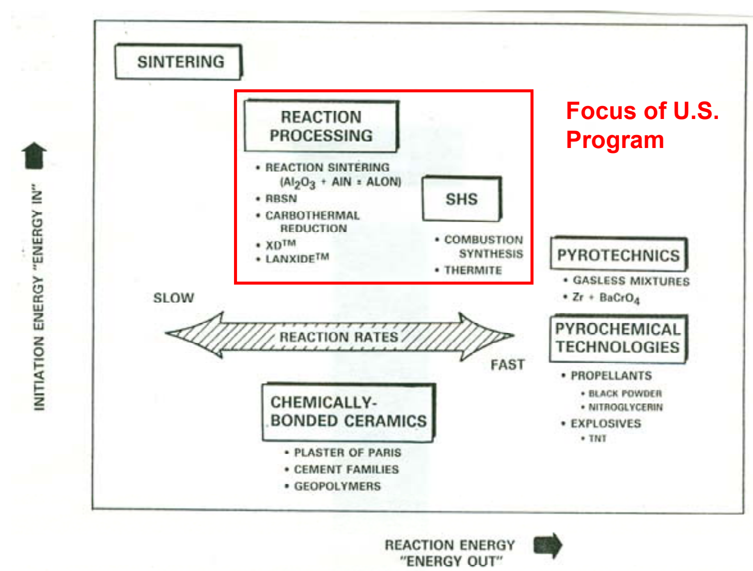
• AMMRC/MTL: N. Corbin, T. Resetar, P. Wong, K. Gabriel, K. Moon, R. Jurta, J. Marzik, L. Carreiro, J. Crider, E. Lenoe, V. Hlavacek, et al.

• Alfred University: G. Stangle, R. Spriggs,

OUTLINE

- Introduction
- Historical perspective in the U.S.: 1976 – 1996; McCauley
- Recent work in the U. S.: 1996 – present; Puszynski

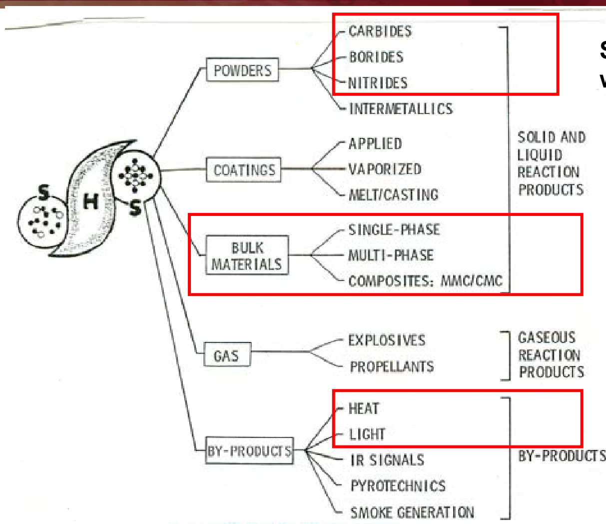
Schematic Representation of Various Exothermic Reactions



Related Technology

- PLASTER OF PARIS
  - $CaSO_4 \cdot 1/2\ H_2O + 3/2\ H_2O = CaSO_4 \cdot 2\ H_2O$
- FAMILY OF CEMENTS
  - $3\ CaO \cdot SiO_2 + 2\ CaO \cdot SiO_2 + H_2O$ = PORTLAND CEMENT
  - CHEMICALLY BONDED CERAMICS (CBC); D. M. ROY (1987)
- GEOPOLYMERS (J + M DAVIDOVICS, FRANCE, 1988)
  - $(Si_2O_5,Al_2O_2)_n + 3n\ H_2O + (NaOH/KOH) \rightarrow$
  - (Na or K) [n $(OH)_3$ Si-O-Al $(OH)_3$] POLY(SIALATE)
- CONTINUUM EXISTS BETWEEN LOW TEMPERATURE (LOW ACTIVATION ENERGY) AND HIGH TEMPERATURE (HIGH ACTIVATION ENERGY) MATERIAL PROCESSING SYSTEMS
- CONTINUUM EXISTS BETWEEN LOW REACTION ENERGY AND HIGH REACTION ENERGY MATERIAL PROCESSING SYSTEMS

True Scope of Self-propagating High Temperature Synthesis - SHS



Second Stage with DARPA

Second Stage at AMMRC/MTL

First stage at AMMRC

Coming to consensus on identifiable acronym for this technology: SHS

Generalized Overall History of SHS in U. S.: 1976 - 1989

- FIRST STAGE:
  - WALTON and POULOS (U.S.) 1959 - CERMETS FROM THERMITE REACTIONS - NO IMMEDIATE FOLLOW-UP IN U.S.
  - BOROVINSKAYA, SHKIRO, and MERZHANOV - CONTINUOUS WORK SINCE 1967 IN RUSSIA (>150 PAPERS PUBLISHED)
- SECOND STAGE: (OUTSIDE OF RUSSIA)
  - UNITED STATES:
    - 1977-1982: McCAULEY, CORBIN, RESETAR et al. ON $Zr + BaCrO_4$ AND Ti-B-C REACTIONS
    - 1982-ON: HOLT, MUNIR, LOGAN et al.
    - SYMPOSIA:
      - JANUARY 1982: COCOA BEACH; VERY SMALL
      - DECEMBER 1983: ARMY/DARPA SHS WORKSHOP
      - MAY 1985: SESSION AT ANNUAL ACerS MEETING
      - OCTOBER 1985: DARPA/ARMY SHS SYMPOSIUM
      - OCTOBER 1988: INTERNATIONAL SYMPOSIUM
    - REVIEWS:
      - CRIDER, 1982
      - FRANKHOUSER et al., 1983 & 1985
      - HARDT, 1984
      - FRANKHOUSER, 1987
      - GABRIEL, WAX, and McCAULEY, 1987

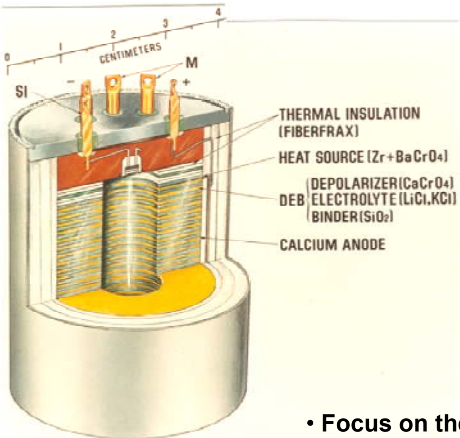
Joey F. Crider, Self-propagating High Temperature Synthesis – A Soviet Method for Producing Ceramic Materials: 6th Annual Conference on Composites and Advanced Materials, Cocoa Beach, Fl., Jan. 1982 (Cer. Eng. And Science Proceedings, V.3, No. 9-10, 1982).

Short History: McCauley Perspective

- Army Materials and Mechanics Research Center/ Materials Technology Laboratory: 1975-1989
  - Thermal battery heat paper – Zr + air and $Zr + BaCrO_4$ reactions
  - SHS for processing ceramics – Ti + B and $Ti + B_4C$
  - Initiation and management of a major DARPA program
  - Interactions with Japan and Russia begin
  - McCauley works in Tokyo, Japan 1988 – interacts with all SHS groups
  - Organizing several workshops and International symposia
- Alfred University: 1990 – 1996

Thermal Battery Heat Paper

Optimize Performance of Zr Powder Heat Paper in Thermal Batteries



"Gasless" Reactions

- $Zr + (AIR) \rightarrow ZrO_2$
- $Zr + BaCrO_4 + (AIR)$
  - $3\ Zr + 4\ BaCrO_4 \rightarrow 3\ ZrO_2 + 4\ BaO + 2\ Cr_2O_3$
    $3\ ZrO_2 + 3\ BaO \rightarrow 3\ BaZrO_3$
  - $3\ Zr + 2\ BaCrO_4 \rightarrow 3\ ZrO_2 + 2\ BaO + 2\ Cr$
    $3\ ZrO_2 + 2\ BaO \rightarrow 2\ BaZrO_3$

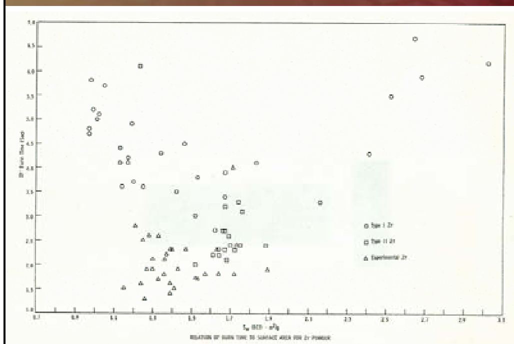
HEAT OF REACTION:

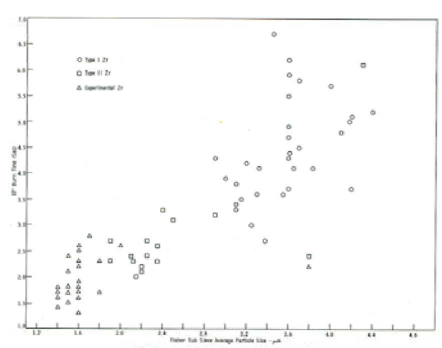
15 - 50 WT% Zr — 273-502 cal/g
85 - 50 WT% $BaCrO_4$

502 cal/g for ~ 60 WT% $BaCrO_4$

- **Focus on the Chemical and Physical Characteristics of Zr powder and their affect on burning characteristics**

Zr Burn Time Relationships





COMPARISON OF PREDICTED TO OBSERVED BURN TIMES

EQUATION (1) BT(Sec) = 1.35 (FSSS) - 0.44

EQUATION (2) BT(Sec) = 5.68 - 1.99 (S_w) + 0.20 (d_g) - 0.05 (Δ')

Sample	Type	BURN TIME (10") OBS Sec	CALC (1) Sec	CALC (2) Sec
5092 A-3	VENTRON I	4.8	5.1	4.9
5042 A-2	VENTRON II	2.6	2.7	2.6
L-10	EPI	1.8	1.6	3.3
L-20	EPI	2.3	1.7	3.4
L-33-T	EPI	1.7	1.6	3.4
L-38-T	EPI	1.6	1.7	3.7

- **Relation of burn time to Fisher Sub Sieve is clear (measure of size and surface area – permeametry number)**
- **No apparent relation to surface area**
- **Large surface area powders have more surface oxygen, which slows down burn rate**

Zr Powder Characterization Data

I.D.	Physical						Chemical		Oxygen Content (w%)		Property
Sample	Sedigraph $d_g(50\%)$ (μm)	Sedigraph $\sigma_g(84,16)$	$\sigma_g(84)$-$\sigma_g(16)$	Sw (BET) (m^2/g)	FSSS APS (μm)	Sw(BET)/Sw(d_g)	% Free Zr	% Mg	Leco	Neut. Act.	sec/10" (Burn Time)
J5078A-1	3.15	1.75	0.23	1.23	4.3	4.22	-		4.32	2.646	6.1
J5068A-3	1.88	1.64	0.15	1.74	2.4	3.56	89	-	4.43	3.503	3.3
J5068A-4	1.92	1.69	0.17	1.76	2.5	3.68	88.8	-	4.72	3.563	3.1
J5116A-1	1.89	1.65	0.15	1.67	2.9	3.44	88.9	-.	4.82	3.575	3.2
J5068A-1	1.87	1.71	0.27	1.67	1.9	3.4	86.1	-	4.86	--?--	2.7
J5042A-1	1.8	1.6	0.2	1.67	2.35	3.27	87.7	-	4.95	3.933	2.3
J5042A-3	1.85	1.57	0.13	1.64	2.2	3.3	87.4	-	4.95	3.89	2.2
J5043A-4	1.75	1.65	0.17	1.72	2.12	3.27	87.1	-	5	3.880	2.3
J5116A-2	1.89	1.73	0.15	1.75	3.8	3.6	88.7	-	5	3.773	2.4
J5043A-1	1.85	1.67	0.2	1.52	2.15	3.06	88.5	-	5.01	3.723	2
J5043A-2	1.88	1.61	0.22	1.61	2.2	3.29	87.1	-	5.04	3.912	2.2
J5042A-4	1.75	1.67	0.29	1.68	2.2	3.2	87.7	-	5.08	4.072	2.1
J5065A-1	1.8	1.65	0.32	1.70	2.25	3.33	87.4	-	5.15	3.969	2.4
J5051A-1	1.85	1.69	0.29	1.66	2.25	3.34	87.9	-	5.26	3.855	2.7
J5043A-3	1.8	1.54	0.4	1.88	2.1	3.68	87.7	-	5.41	4.065	2.4

SORTED ACCORDING TO ASCENDING LECO OXYGEN CONTENT

Figure 8. Powder Characterization Data Set for Zr Metal

DARPA Advanced Materials Program
1984 -1986: ~ $1.7 M

- **Overall contract manager: J. W. McCauley**
- **Program breakdown:**
  - **Prime contractor: Lawrence Livermore National Laboratory**
  - **Program manager: J. Birch Holt**
  - **Focus: Combustion synthesis and plasma chemical synthesis**
  - **Sub-contractors:**
    - **University of California, Davis, Ceramatec, Los Alamos National Laboratory and Rice University**

- **First major review in the U.S. of on-going work:**

"Materials Processing by Self-propagating High-temperature Synthesis (SHS)"; K.A. Gabriel, S.G. Wax and J.W. McCauley, eds., Proceedings of DARPA/Army SHS Symposium, 21-23 Oct. 1985, Daytona Beach, Fl. MTL SP 87-8.

Focus of Symposium

- DARPA SHS program review: LLNL, UC Davis, LANL, Rice, Ceramatec, Ohio State,
- Low pressure processes,
- Modeling and characterization techniques,
- Synthesis techniques,
- SHS surface related processes,
- General materials processing.

Materials Technology Laboratory
Shift from Using By-products of SHS to Processing

Focus of Program

- **Utilize reaction sintering concepts without pressure**
- **Importance of physical and chemical characteristics of powders**
- **Focus on phase equilibrium**
- **Detailed characterization of final sintered products**

SHS Characteristics

	INFLUENCED BY PRECURSOR PHYSICAL CHARACTERISTICS	INFLUENCED BY PRECURSOR CHEMICAL CHARACTERISTICS
REACTION	• REACTION RATE • CONDUCTIVE HEAT LOSS • REACTION INITIATION	• ADIABATIC TEMPERATURE • REACTION MECHANISM • Liquid formation • VOLATILE EVOLUTION
PRODUCT	• DENSITIES • MICROSTRUCTURE • UNREACTED MATERIAL	• SECONDARY PHASES • IMPURITY CONTENT • POROSITY

SHS as Reaction Sintering

- Requirements:
  - Removal of porosity arising from:
    - Remnant powder packing, etc.
    - Product density change from reactants
    - Gas as reaction product
  - Propagation/control of reaction

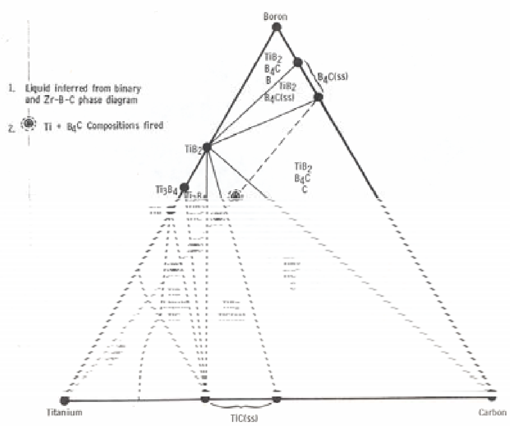
Dependence of Above on Presence and Characteristics of Liquid and Vapor Phases

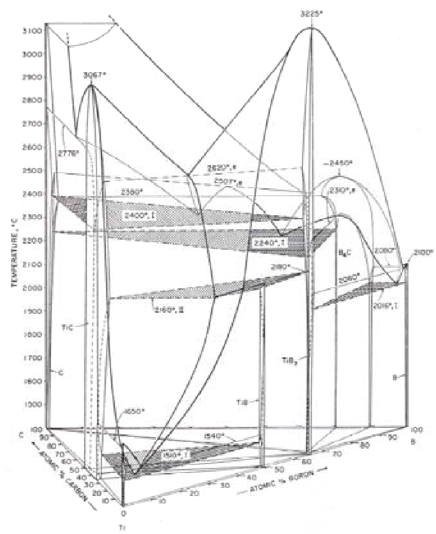
- **Equilibrium Factors:**
  - Phase equilibrium
  - Energies of reaction
- **Non-equilibrium factors (kinetic):**
  - Actual chemistry of reactants: bulk and spatial distribution
  - Physical characteristics of reactants

Some Reaction Sintering Issues

- Chemical driving forces much higher than conventional sintering
- If gas forms most diffuse out
- Volume fractions of reactants and products change with time – density difference
- Kirkendall effects: porosity formation due to density change between reactants and products
- Wetting between liquids and solid phases becomes important
- Grain size reduction from reactants – nucleate new phases

Relevant Phase Equilibrium
Ti- B-C System





Reactants:

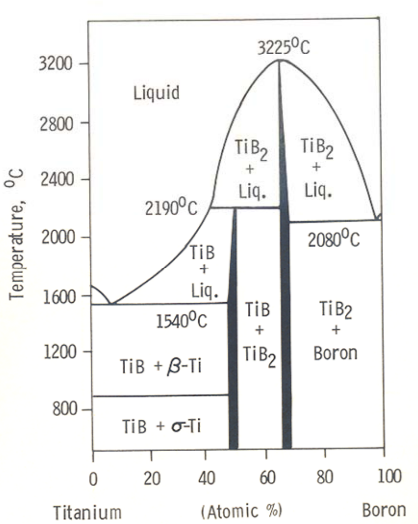
1.) Ti + B

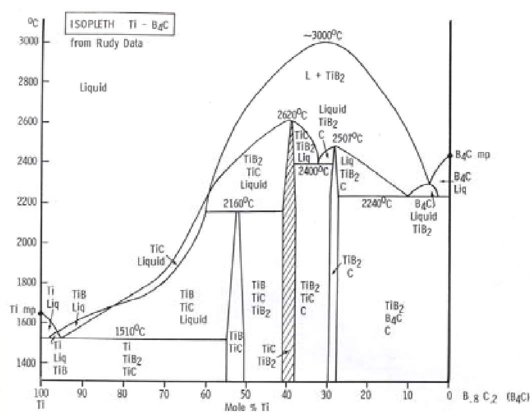
2.) Ti + B + TiB_2

3.) Ti + B_4C

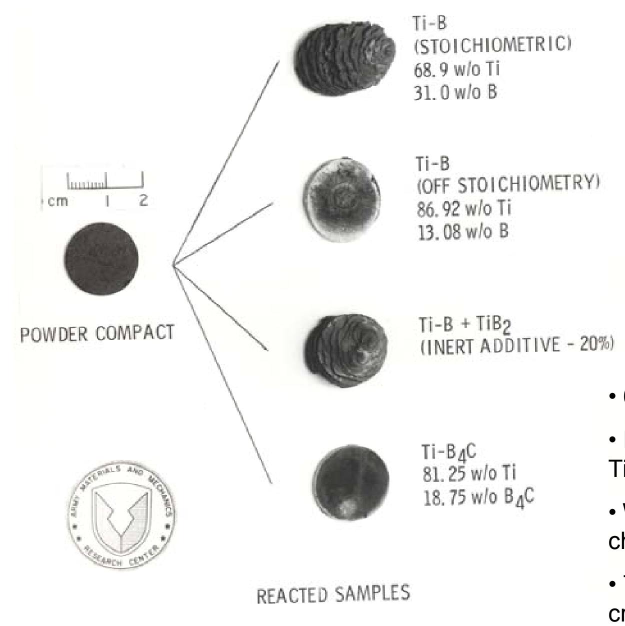
Rudy, 1969

Ti-B and Ti- B_4C Binary Diagrams





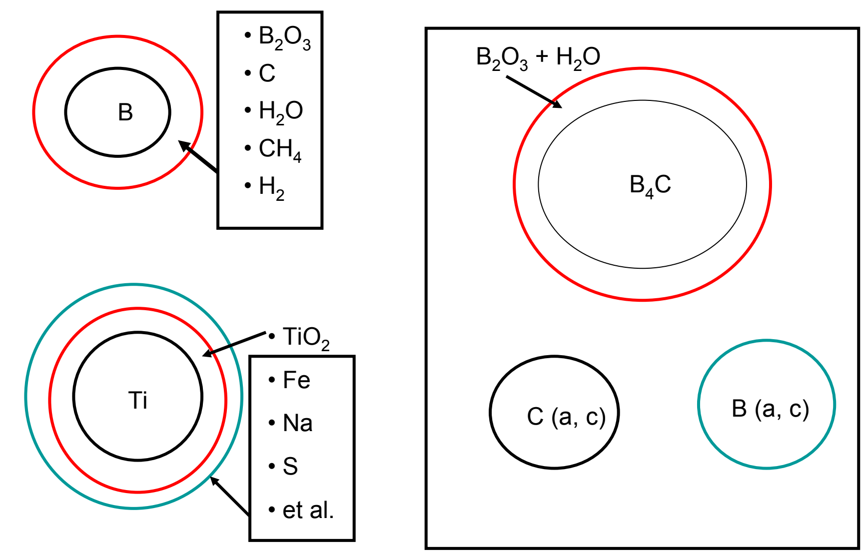
Reacted Samples in the Ti-B-C System



Some Results

- 68 – 85 wt.% Ti + B_4C
- Resulting phases: TiB_2, TiC, Ti_3B_4, TiB, C.
- Wt. loss and burn rate changes
- Ti and B_4C starting powder critical

Powder Chemical Characteristics

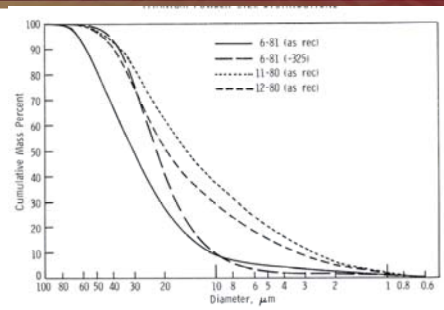


B_4C Powder

Powder Physical Characteristics

- Average particle size
- Particle size distribution
- Surface area and morphology
- Relative size of reactants

Ti Powder Characteristics

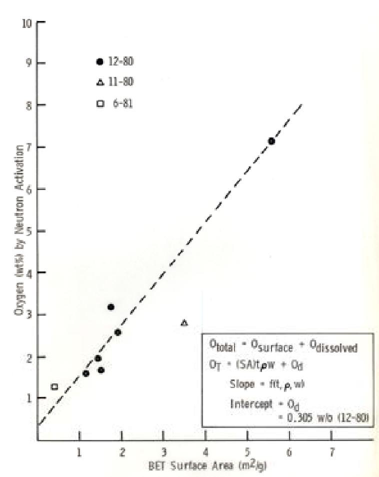


SIEVED TITANIUM (12-80) POWDER

CHEMICAL ANALYSIS*

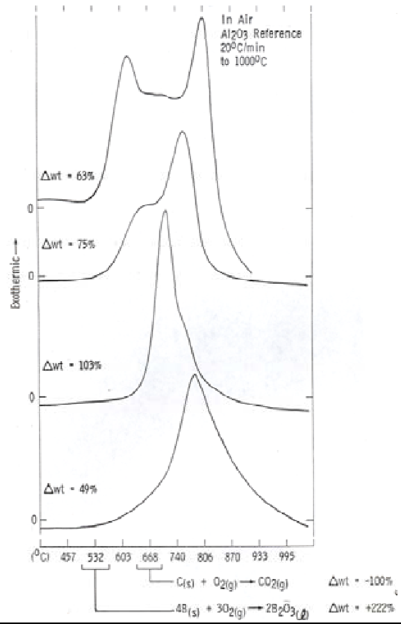
	37μ	30-37	20-37	10-20	<10
Ti	96.0	96.0	96.0	95.0	83.0
Fe	1+	1.5	1+	2.0	9.0
Zn	0.2	0.2	0.2	0.2	0.5
Ni	tr	tr	tr	tr	0.3
Cr	tr	tr	tr	tr	0.2
Cu	tr	tr	tr	tr	tr
Zr					0.1
O	1.63	1.97	1.68	2.56	7.08

*SEMI-QUANTITATIVE BY XRF, OXYGEN BY NEUTRON ACTIVATION



OXYGEN CONTENT VERSUS SURFACE AREA FOR TITANIUM POWDERS

Boron Carbide Characteristics



Chemical

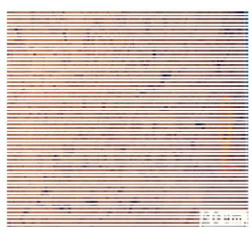
- Phases: B_4C, B_a, B_c, B_2O_3, H_2O
- Differential thermal analysis

Physical

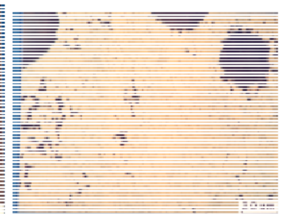
- Surface areas: 0.76 – 4.81 m2/g
- Median particle size: 2.5 – 20 µm
- Particle size distribution: < 1 µm

Boron Characteristics

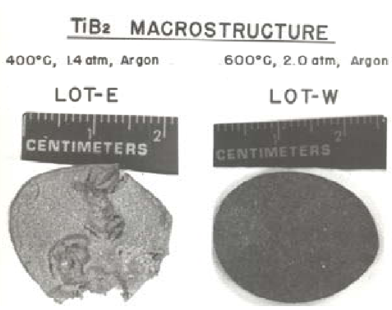
Lot	Wt % O	Total Impurities
W	0.21	0.94
A (38-74 µm)	0.9	1.47
A (<38µm)	1.6	1.47
E	3.76	0
C	24.9	0.58



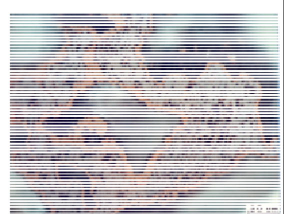
Lot A 0.9 % O



Lot A 1.6 % O

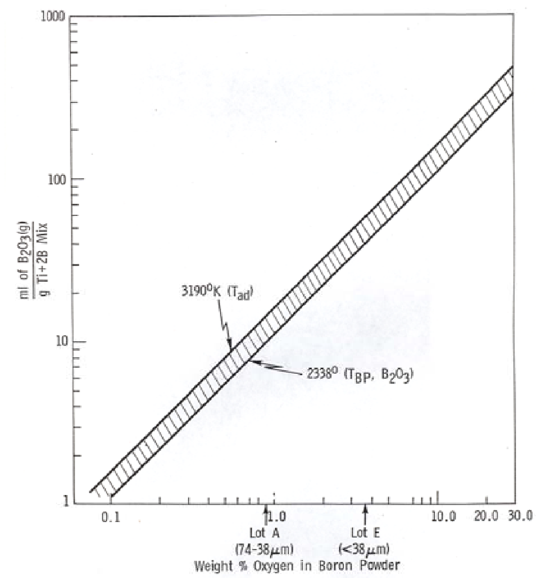


Lot E 3.76 % O



Lot C 24.9 % O

B_2O_3 Gas Evolution from Boron Powder



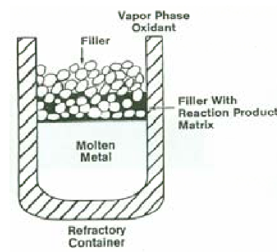
BORON OXYGEN CONTENT VERSUS VOLUME OF B_2O_3 GAS FORMED IN Ti+2B SHS MIXTURE

SHS Groups in US – circa 1990

ORGANIZATION	PRINCIPAL INVESTIGATORS	TECHNOLOGY FOCUS	Current Status
DEPARTMENT OF DEFENSE			
ARMY MATERIALS TECHNOLOGY LAB	CROFT, MARZIK, McCAULEY	POWDER CHAR, SINTERING, PHASE EQ.	No
ARMY BALLISTIC RESEARCH LAB	NIILER, KOTTKE	DYNAMIC COMPACTION, MODELING	No
ARMY RESEARCH OFFICE	CROWSON	COORDINATION, MANAGEMENT	No
DEPARTMENT OF ENERGY			
LOS ALAMOS NATIONAL LAB	BEHRENS	HIGH T CHEM, MODELS	No
LAWRENCE LIVERMORE NATIONAL LAB	HOLT, HALVERSON, CHOW et al.	POWDERS, BULK MAT'LS, MODELS	No
SANDIA NATIONAL LABS (LIVERMORE)	MARGOLIS	MODELING	?
ACADEMIA			
ALFRED UNIVERSITY	SPRIGGS	MAT'LS PROC, REVIEWS	No
OREGON STATE UNIVERSITY	KANURY	MATH MODELS	?
WASHINGTON STATE UNIVERSITY	WOJECKI	MAT'LS PROC, EUTECTICS	?
UNIVERSITY OF CALIFORNIA - DAVIS	MUNIR	MAT'LS PROC, FUNDAMENTALS	Yes
NORTHWESTERN UNIVERSITY	MATKOWSKY	MODELING	?
GEORGIA TECH. RESEARCH INSTITUTE	LOGAN	MAT'LS PROC, POWDERS, THERMITE	Yes
RICE UNIVERSITY	MARGRAVE	HIGH T MASS SPEC	No
NEW MEXICO INST. OF MIN. & TECH.	THADHANI	EXPLOSIVE COMPACTION	Yes
STATE UNIV. OF NEW YORK - BUFFALO	HLAVACEK, PUSZYNSKI	POWDERS, FIBERS, MAT'LS, MODELS	No/yes
UNIV. OF CALIFORNIA - SAN DIEGO	MEYERS	EXPLOSIVE COMPACTION	No
UNIVERISTY OF FLORIDA	CLARK, DALTON	MICROWAVE PROCESSING	No
COLORADO SCHOOL OF MINES	MOORE	INTERMETALLICS	?
INDUSTRY			
RESEARCH TRIANGLE INSTITUTE	MULLINS	FIBERS + MMC	No
CERAMETEC	CUTLER	POWDERS, MAT'LS THERMITE	No
GENERAL SCIENCES INC.	ZAVITSANOS	LOW PRESSURE PROCESSING	Yes
SYSTEM PLANNING CORP.	FRANKHOUSER	REVIEWS, ANALYSIS	No
LOCKHEED	HARDT	SINTERING, PHASE EQUILIBRIA	No
CORNING GLASS WORKS	DeANGELIS	REACTION HOT PRESSING	No
N.J. DAMASKOS, INC.	SENFT	PROCESSING	No
W.R. GRACE	RICE	MAT'LS PROC	No
ADVANCED REFRACTORY TECHNOLOGIES	BLAKELY	POWDERS + WHISKERS	No
BENCHMARK STRUCTURAL CERAMIC CORP.	HIDA	POWDERS/WHISKERS BLENDS	
POWDER TECHNOLOGIES INC.	LOGAN	POWDERS, BULK MATERIALS	Yes
SYNERGETIC MATERIALS INC.	HALVERSON	ADVANCED MATERIALS	No
KISER RESEARCH INC.	KISER	SOVIET SHS TECHNOLOGY	No

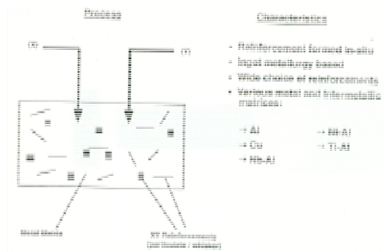
Related Processing Technology

- REACTION-BASED PROCESSING -
  CHIANG, HAGGERTY et al. AT MIT
- XD™ PROCESSING OF METAL MATRIX COMPOSITES -
  CHRISTODOULOU, BRUPBACHER, and NAGLE AT MARTIN MARIETTA
- LANXIDE™ CERAMIC COMPOSITE MATERIALS -
  NEWKIRK, URQUHART et al. AT LANXIDE CORPORATION
- OTHERS -
  CARBOTHERMAL REDUCTION, REACTION-BONDED SILICON NITRIDE (RBSN), etc.



Newkirk et al., “Preparation of LANXIDE™ Ceramic Matrix Composites, Cer. Eng. Proc., v. 8, 1987.

XD™ Process for Producing Metal Matrix Composites – Martin Marietta



Important International Activities 1988 - 1993

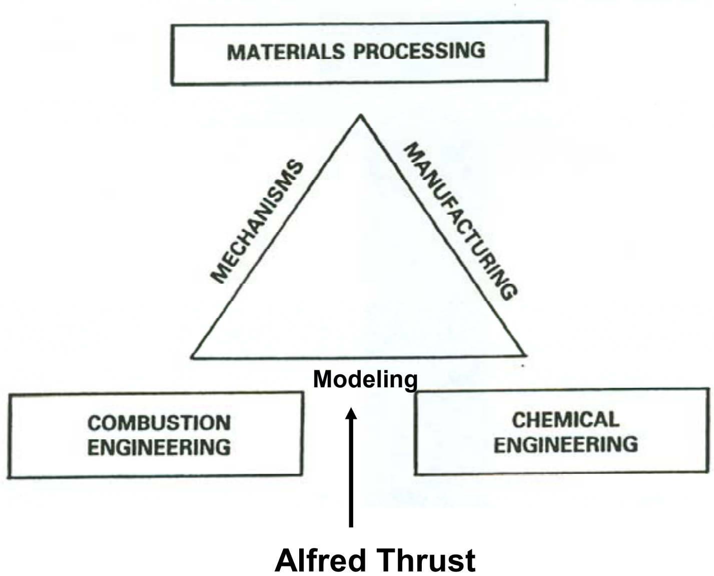
- 1988: Symposium on SHS; San Francisco, CA
- 1988: Formation of Japanese Research Association for Combustion Synthesis – Koizumi and Miyamoto
- 1988: McCauley assignment in Tokyo, Japan – major focus is SHS and FGM
- 1989: Kiser Research Inc. special meeting, Arlington, Va. “Soviet Advances in High Performance Ceramics using Solid Flame Technology”.
- 1990: Tsukuba Science City, Japan
- 1991: First International Symposium on SHS Alma-Ata, Kazakhstan
- 1991: US-USSR SHS Workshop, Alfred University
- 1993: Second International Symposium on SHS, Honolulu, Hawaii
- 1993: Formation of “American Association of Combustion Synthesis” Munir

Time Period During Transition to Alfred University

• "An Historical and Technical Perspective on SHS": J.W. McCauley, Ceram. Eng. Sci. Proceedings. 11, [9-10] 1137-1181, (1990).

• "Combustion Synthesis: A Historical Perspective", V. Hlavacek, Cer. Bull., 70,[2] 240-243 (1991).

Optimization for Materials Processing Requires a Unification of Approaches



Alfred University: 1990 – 1996

- Focus on modeling and Functionally Graded Materials
- Interactions and formal agreement with NRIM, Japan (Kaieda)
- Formal agreement with the Institute of Materials Science, School of Mining and Metallurgy, Poland (Pampuch)
- Interactions with ISMAN (Merzhanov and Borovinskaya)

April 1991 Alfred Workshop

SOVIET scientists visit the Alfred University campus.

ISMAN/Alfred Collaboration Agreement Signed October 1990

Dean James W. McCauley (r) and Professor Alexander G. Merzhanov of the USSR Institute of Structural Macrokinetics (ISMAN) sign three-year agreement to study Self-Propagating High-Temperature Synthesis jointly with researchers at the New York State College of Ceramics.

US - USSR SHS Workshop, Alfred University

April 4-5, 1991 – McCauley's home

Summary of Alfred Work
1990 - 1996

• Institute for Self-Propagating High-temperature Synthesis (SHS) formed at Alfred: Professor Greg Stangle named Director.

• PIs: Greg Stangle, Dick Spriggs and Jim McCauley

• Stangle: 16 B.S. students

M.S.:

•1995 - Boisvert, Scot M., Fabrication of dense MoSi2 and MoSi2 composites by combustion synthesis

• 1994- Huang, Dai, Combustion synthesis and fast-firing of nanocrystalline yttria-stabilized zirconia

• 1993- Niedzialek, Scott E., The fabrication of functionally gradient materials by the self propagating high-temperature synthesis method

• 1993- Coy, Michael A., Development of a centrifugal-SHS process and analysis of its fabrication capabilities

Ph.D.

• 1996-He, Cheng,An investigation of mechanism and kinetics of combustion synthesis of materials

• 1994- Zhang, Yangsheng, A study of the combustion synthesis process for materials fabrication

• 31 publications

Focus of Alfred Research

• Ultra-fine powder synthesis: Zirconia, YIG, Barium hexaferrite

• Micro-mechanistic models: modes and mechanisms of ignition

• Micro-mechanistic model of combined combustion synthesis densification process

• Near net shaped alumina fiber- reinforced Ni_3Al composites

• Niobium-carbon reactions

• Mo-Si reactions

• Centrifugal-SHS processes

• Functionally Graded Materials (FGM)

Micromechanistic Models and Nb-C System

• Development of quantitative micromechanistic models: theory and numerical simulation – Zhang and Stangle.

- microstructural details derived primarily from percolation concepts as applied to porous media; allows for processing-microstructure-property relationships
- fundamental understanding and precise control of the process depends strongly on the joint contributions of the ***rates*** of the various mass and energy redistribution processes that occur during the combustion synthesis process; a proper balance of each is required for self-propagating behavior.

• Nb-C model system: using reaction couples of thin Nb foils or wire – He and Stangle.

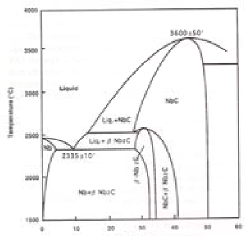
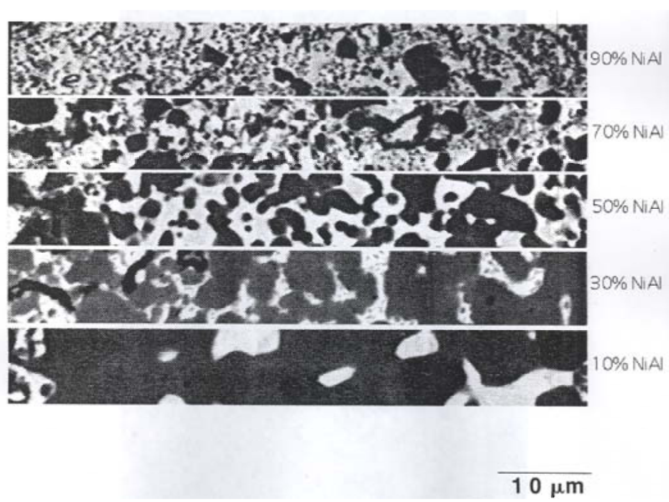


FIG. 1. The Nb–C phase diagram.

- both solid-solid and controlled amount of liquid formation
- no liquid phase – diffusion controlled mechanisms and products
- liquid formation – allows much larger fraction of the reactants to mix at greater rates
- CS/SHS not really “reactions” in the strict sense, but a sequence of chemical and physical processes: melting, dissolution, diffusion and nucleation and growth of the product phases.

Functionally Graded Materials (FGM) at Alfred



TiC – NiAl FGM; S. Niedzialek, G.C. Stangle and Y. Kaieda, 1992

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Appendix B. Oral Presentation: Part 2

From the "International Conference on Historical Aspects of SHS in Different Countries," 22–27 October 2007, Chernogolovka, Moscow, Russia. Historical perspective and contributions of U.S. Researchers into the Field of Combustion Synthesis (SHS): Personal Reflections—recent work; Jan A. Puszynski.

The viewgraphs in this appendix appear in their original form, without editorial change.

SHS - 40
Research Center RAN
Chernogolovka, Russia
22-24 October 2007

Historical Perspective and Contribution of U.S. Researchers into the Field of Combustion Synthesis (SHS)
PART 2: Recent Work

James W. McCauley, Army Research Laboratory, U.S.

and

Jan A. Puszynski, South Dakota School of Mines and Technology, U.S.

CURENT R&D ACTIVITIES AT U.S. UNIVERSITIES

- **University of California at Davis: Professor Z. Munir**
- **Northwestern University: Professor B. Matkowsky and V. Volpert**
- **University of Notre Dame: Professor A. Mukasyan**
- **University of California at San Diego: Professors Meyers and Olewsky**
- **Georgia Institute of Technology: Professor N. Thadani**
- **University of Houston: Professor D. Luss and Dr. K. Martirosyan**
- **Purdue University: Professor A. Varma**
- **Colorado School of Mines: Professor Moore**
- **S.D. School of Mines and Technology: Professor J. Puszynski**
- **University of Nebraska: Professor H. Viljoen**
- **University of Southern Mississippi: Professor J. Pojman**
- **Princeton University: Professor C. Law**
- **University of Illinois: Professor K. Brzezinski**
- **John Hopkins University: Professor T. Weih**
- **New Jersey Institute of Technology: Professor E. Drezin**

Professor Zuhair Munir

- Analysis of the origin of porosity in SHS products (1993).
- The role of electric fields in SHS reactions: Modeling and experimental work (1995-1998).
- Separation of the thermal (Joule heat) from the intrinsic (electron wind effect) contributions of the field (current), work on electromigration has demonstrated field effect on point defect generation and mobility (2001).
- Recent work on the combined mechanical and field activation to synthesize dense (bulk) nano-ceramics and nano-composites in one step (2001-present).
- Use of field activation for simultaneous synthesis and consolidation of complex materials (Ti_2SiC_3 (1999), TiB_2-WB_2-CrB_2 (2001), AlN-SiC (1996-2000).
- Use of field activation for microalloying (2003-2004).
- Use of field activation to prepare nanostructured functional oxides for fuel cell applications: Novel demonstration of power generation at room temperature by protonic conduction.

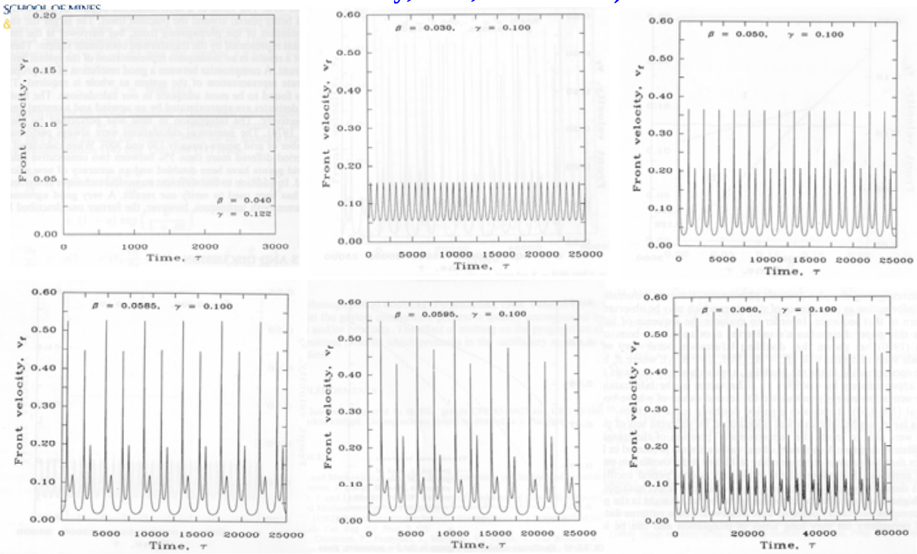
Professor Zuhair Munir

Professor Munir has collaborated with Professors:

- Frederic Bernard, University of Burgundy, Dijon, France;
- Manshi Ohyanagi, Ryukoku University, Seta, Japan;
- Umberto Anselmi-Tamburini, University of Pavia, Italy;
- Giacomo Cao, University of Cagliari, Italy;
- Manfred Martin, University of Aachen, Germany;
- Rainer Telle, University of Aachen, Germany;
- In-Jin Shon, Chonbuk National University, Korea;
- Myeong-Woo Cho, Inha University, Korea;
- Roberto Tomasi, Sao Carlos Federal University, Brasil;
- Qing-sen Meng Taiyuan University of Technology, China;
- K. A. Khor, Nanyang Technological University, Singapore.;
- Z. Y. Fu, Wuhan University of Technology, China;
- Yu. Maksimov, Tomsk University, Russia.

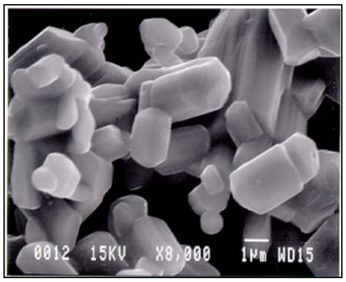
He has also ongoing collaboration with U.S. national laboratories, including collaboration with Dr. Alex Gash from Lawrence Livermore National Laboratory, USA and Dr. John Neal from Oak Ridge National Laboratory, USA.

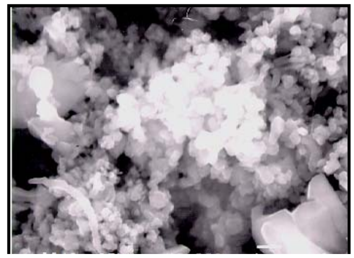
Mathematical Modeling of SHS Processes (Matkowsky, Volpert, Hlavacek, Puszynski, Viljoen, Olewsky, Law, and Varma)

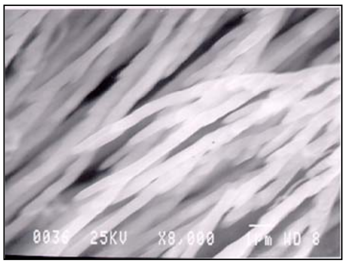


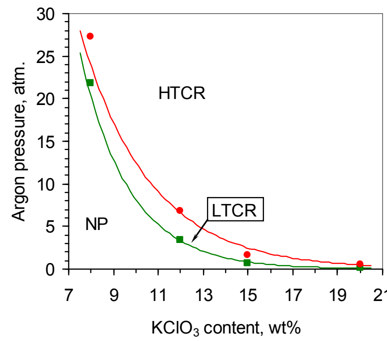
Mathematical Modeling of SHS Processes (Matkowsky, Volpert, Hlavacek, Puszynski, Viljoen, Olewsky, Law, and Varma)

Professor Puszynski
Si_3N_4 and SiC: Chemically-enhanced SHS

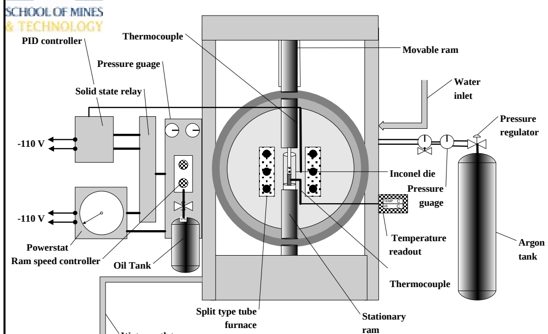


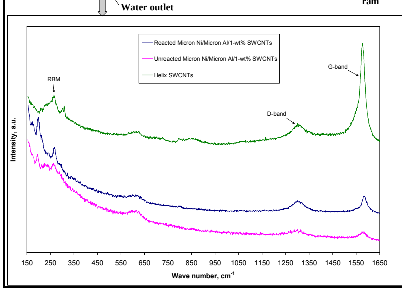


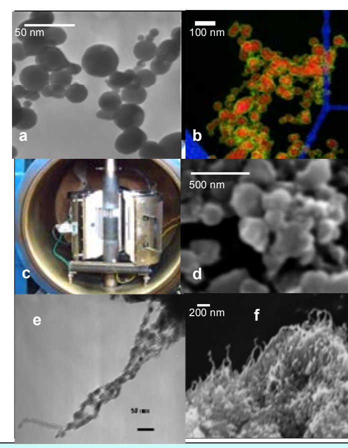




Professor Puszynski: Simultaneous Combustion Synthesis and Densification of Nanocomposites

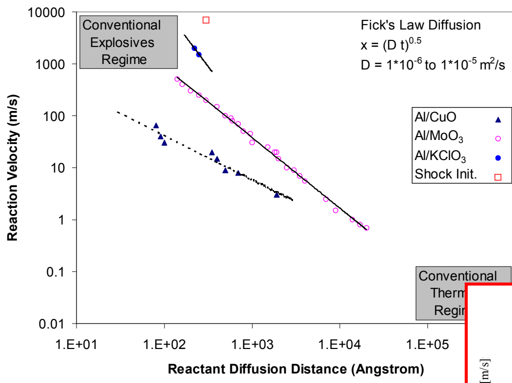


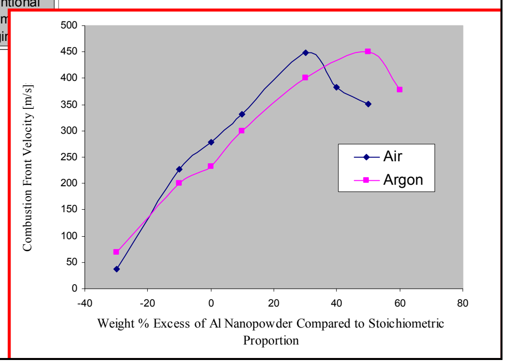




a) and b) TEM images of Al and Ni nanoreactants, c) reaction chamber, d) SEM image of nanosize nickel aluminide-alumina composite prepared by simultaneous combustion synthesis and densification, e) and f) SEM images of single-walled carbon nanotubes reinforced nickel aluminide-alumina nanocomposites.

Professor Puszynski
NANOTHERMITE REACTIONS





Professor Puszynski
Combustion Front Propagation
Both Tube Ends Open

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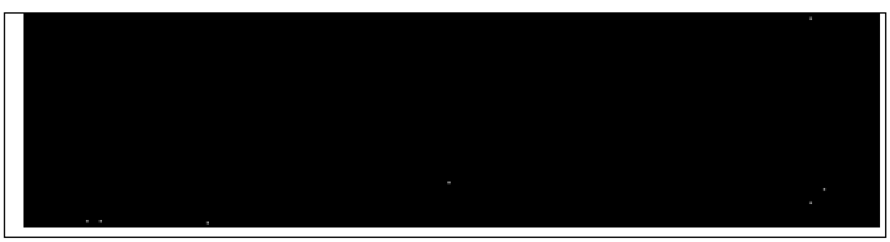
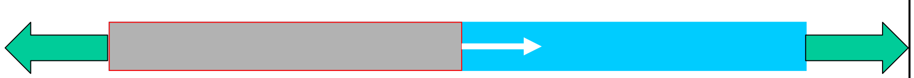
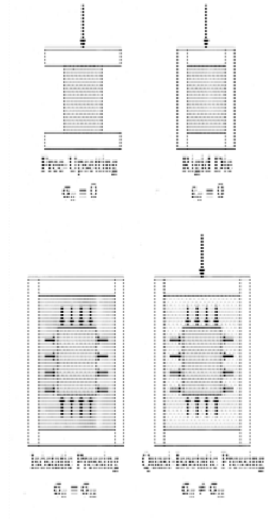




Professors M. Meyers and Olewsky



- **Shock Consolidation**
- Similar to pressing in a rigid die;

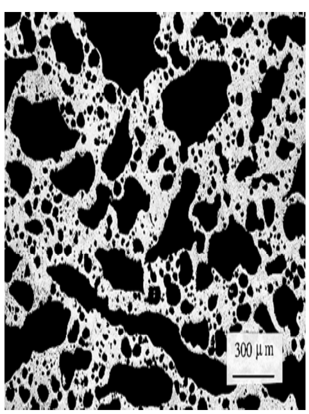
$$\varepsilon_{rr} = 0$$

- **Impact Forging**
- Again, similar to pressing in a rigid die
- **Quasi-Isostatic Pressing (QIP)**

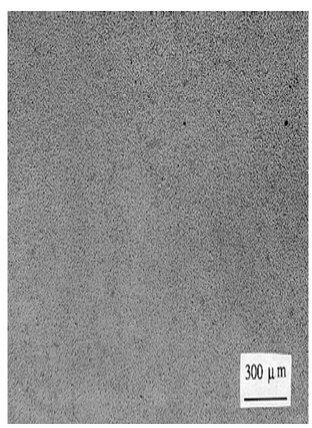
$$\sigma_{rr} \neq \sigma_{zz}$$

Professors M. Meyers and Olewsky

- As-reacted TiC Cermet

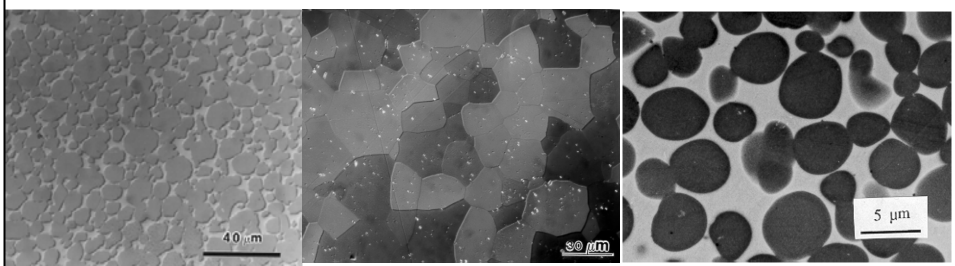


- Densified TiC Cermet (QIP)



Professors M. Meyers and Olewsky

TiC TiC-25%Ni TiC-NiTi

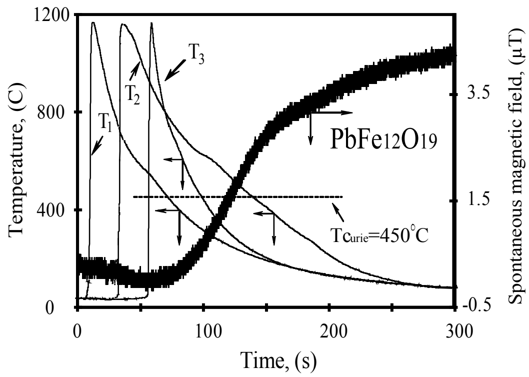


Professors Varma and Mukasyan

- **Combustion synthesis of nanomaterials with different applications e.g. hydrogen production (combustion solution technique).**
- **Joining of carbon-carbon composites.**
- **Mechanism of heterogeneous combustion.**
- **SHS in microgravity.**
- **Mathematical modeling.**

Drs. Luss and Martirosyan

- Carbon combustion synthesis of oxides.
- Spontaneous magnetization during solid phase reaction.



U.S. INDUSTRY

- Advanced Refractory Technologies, Inc.*
- Reactive Nanofoils, Inc.
- Blash Ceramics, Inc.
- Advanced Materials, Inc.
- Exotech, Inc.

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Acknowledgment

The authors acknowledge his colleagues, Professors Munir, Luss, Pojman, Mukasyan, Matkowsky, Volpert, Viljoen, Law, and Meyers for providing information and research material for this presentation.

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Thank you

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10	NATL INST OF STANDARDS & TECH CRMCS DIV G QUINN STOP 852 GAITHERSBURG MD 20899
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ABERDEEN PROVING GROUND

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